

**Corrosion Inhibitor Surfactant Optimization:
Part 2 – Adsorption Kinetics Approach**

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ABSTRACT

In Part 1 of this two part paper, the critical micelle concentration (CMC) and corrosion inhibitor efficiency response curve was estimated for mixtures relating to the homologous series of alkyldimethylbenzylammonium chlorides with C₁₂, C₁₄ and C₁₆ tail lengths. In the first paper, the uninhibited and inhibited corrosion rates were used to estimate corrosion inhibitor efficiency and were used to determine the optimum mixture ratio of the three surfactants based on their ability to minimize the steady state inhibited corrosion rate. In this second part, the transient data between the uninhibited and inhibited steady state corrosion rate were used to estimate the rate of change of surface coverage. This transient response in coverage was then analyzed using a mixed first and second order adsorption kinetic model, which enabled quantification of the adsorption and desorption rate constants. The adsorption rate constants were determined for the same 10-point three-component simplex mixture experimental design introduced in Part 1. Cubic response curves were calculated for the adsorption and desorption rate constants, and adsorption equilibrium constant. The adsorption rate constant and desorption rate constants were found to have very different interaction strengths, with the adsorption rate constant showing a stronger pairwise interaction, whilst the desorption rate constant displayed a stronger ternary interaction. The differences between the interaction strengths between pairwise and ternary interactions is reflected in the composite equilibrium constant.

Key words: Surfactant, Critical Micelle Concentration, Optimization, Adsorption Kinetics

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INTRODUCTION

In the first paper, a mixture design matrix of a homologous series of alkyldimethylbenzylammonium chlorides (BAC) was used to assess the performance and facilitate optimization of a mixed surfactant corrosion inhibitor system based on surface coverage and steady state inhibited corrosion rate.¹ In this second paper, the approach is extended to include adsorption kinetic analysis, as demonstrated in Woollam and Betancourt for a first-order Langmuir kinetic model.²

The traditional laboratory-based approach when evaluating corrosion inhibitor performance is to track the corrosion rate of steel over time using *in-situ* electrochemical techniques, e.g. linear polarization resistance (LPR). In such instances, typically only the initial, uninhibited rate and the final steady state corrosion rate are extracted to determine an inhibitor efficiency.

The previous study by Woollam and Betancourt describes the application of the Langmuir kinetic model (Equation [1]) in the analysis of corrosion rate vs. time curves,²

$$\frac{d\theta}{dt} = k_a(1-\theta)C - k_d\theta \quad [1]$$

where θ is surface coverage (determined from the drop in corrosion rate as a result of inhibitor adsorption from that of the uninhibited corrosion rate), C is surfactant concentration and k_a and k_d are the adsorption and desorption rate constants, respectively. The paper demonstrates that fitting the full transient dataset to a kinetic model provides deeper insight into corrosion inhibitor performance. The approach generates not only the steady-state parameters provided by traditional methods, i.e. K_L where $K_L = k_a / k_d$, but also kinetic parameters related to adsorption and desorption processes, k_a and k_d . Furthermore, to determine these parameters, it is not necessary for the experiment to reach a pseudo-steady state, as the steady state parameters are derived based on the kinetic parameters themselves, since $K_L = k_a / k_d$.

Overall, the approach provides a greater insight into inhibitor characteristics, producing a number of additional parameters for quantification, comparison, and optimization of corrosion inhibitor performance.

Extension of Previous Study using Mixed-Order Kinetics

For this study, the simple first-order Langmuir model used previously (and applied to single inhibitor components) was extended to use the mixed order model of Marczewski, demonstrating its applicability to inhibitor blend optimization for a homologous series of BACs consisting of three tail lengths, $n = \{C_{12}, C_{14} \text{ and } C_{16}\}$.³ The model structure is,

$$\frac{dF}{dt} = k_1(1-F) + k_2\theta_{ss}(1-F^2) \quad [2]$$

where k_1 and k_2 are the first and second order pseudo rate constants, respectively, and F is the fractional attainment of equilibrium coverage, θ_{ss} , such that,

$$F = \frac{\theta}{\theta_{ss}} \quad [3]$$

The pseudo-rate constants can be combined into a single rate constant and a weighting factor, f_2 , such that for $f_2 = 0$ the system is a pseudo first order model, and for $f_2 = 1$ the system is a pseudo second order model. The integrated form of Equation [2] then becomes,

$$\ln \left(\frac{1-F}{1-f_2 F} \right) = -k_1 t \quad [4]$$

$$\theta = \theta_{ss} \frac{1 - e^{-k_1 t}}{1 - f_2 e^{-k_1 t}} \quad [5]$$

where θ is the surface coverage, θ_{ss} is the equilibrium or steady state surface coverage (that is the maximum surface coverage attained as $t \rightarrow \infty$), k_1 is the pseudo adsorption rate constant, and f_2 is the weighting factor between first and second order kinetics.

EXPERIMENTAL METHOD

The experimental methods are detailed in Part 1, however, in summary,¹

- **Homologous Series:** A homologous series of surfactants were used to simulate a multicomponent surfactant system as a corrosion inhibitor. The series consisted of BAC single component surfactant molecules using the same head group with tail lengths of C₁₂, C₁₄ and C₁₆, and summarized in Table 1.
- **Mixture Matrix:** A 10-run formulation mixture matrix was used with individual compositions shown in Table 2. The matrix consists of the three pure components, 3 binary blends and 4 ternary blends.
- **Critical Micelle Concentration (CMC):** The CMC corresponding to each of the mixtures was determined spectroscopically using the lipophilic dye Nile Red. The corrosion performance of each mixture was evaluated at its respective CMC concentration, shown in Table 2.
- **Corrosion Rate Profile:** The test solution consisted of 1 wt.% NaCl under 1 bar of CO₂ at 30°C. The corrosion rate was measured prior to the introduction of each surfactant mixture for 30 minutes, and subsequent to the addition of the corrosion inhibitor to yield a time series/transient corrosion rate profile. The corrosion rate was measured semi-continuously using LPR.

Table 1: Homologous Series Description

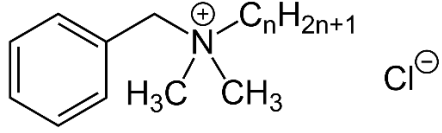
Acronym	Full Name	n	Structure
C ₁₂	Benzyltrimethyl-dodecylammonium chloride	12	
C ₁₄	Benzyltrimethyl-tetradecylammonium chloride	14	
C ₁₆	Benzyltrimethyl-hexadecylammonium chloride	16	

Table 2: Summary of Mixture Composition, CMC Measured and Predicted for 10 Test Matrix

Mixture Number	Mole Fractions			Single Component CMC Measurement (μM)	Multi-Component Ideal Mixture CMC Prediction (μM)	Multi-Component CMC Measurement (μM)
	C12	C14	C16			
1	1	0	0	1000	-	-
2	0	1	0	149.9	-	-
3	0	0	1	17.5	-	-
4	½	½	0	-	260.7	185.5
5	½	0	½	-	34.4	38.9
6	0	½	½	-	31.3	64.5
7	⅓	⅓	⅓	-	46.3	71.9
8	⅔	⅙	⅙	-	88.5	90.0
9	⅙	⅔	⅙	-	70.7	56.0
10	⅙	⅙	⅔	-	25.4	23.6

As noted, a detailed description of the experimental methods can be found in the companion paper.¹

RESULTS AND DISCUSSION

In the first paper, the performance of the corrosion inhibitor was assessed using the corrosion inhibitor efficiency, calculated as,

$$CI_{Eff} = 1 - \frac{CR_{In}}{CR_{Un}} = \theta_{ss} \quad [6]$$

As has been noted elsewhere, this approach utilizes only a small portion of the corrosion rate transient since it considers only the initial uninhibited corrosion rate, CR_{Un} , and the nominal steady-state inhibited corrosion rate at the conclusion of the test.² This results in the majority of the transient corrosion rate information being excluded from this form of analysis.

In order to obtain more detailed information regarding the kinetics of adsorption, the transient corrosion response is utilized to gain greater insight.

Surface Coverage with Time

The adsorption kinetics can be obtained by converting the transient corrosion rate profile into a surface coverage profile using Equation [6] in its transient form to yield,

$$\theta_t = 1 - \frac{CR_t}{CR_{Un}} \quad [7]$$

where θ_t is the transient surface coverage at time t , CR_t is the transient corrosion rate at time t , and CR_{Un} is the initial uninhibited corrosion rate obtained at the start of the experiment prior to surfactant injection. In addition to the transformation of the corrosion rate to surface coverage, the time base is reset to give $t = 0$ as the point at which the corrosion inhibitor/surfactant mixture is injected.

Examples of corrosion rate profiles are shown in Figure 1, with Figure 1(a) showing the corrosion rate profile for the pure component C₁₆, and Figure 1(b) showing the corrosion rate profile for a mixed component surfactant, Mixture 9, consisting of 1/6, 2/3 and 1/6 of the C₁₂, C₁₄ and C₁₆, respectively. Both tests were performed at their experimentally determined CMC provided in Table 2.

Using Equation [7], the transformed version of these corrosion rate profiles are shown as the surface coverage, θ , in Figures 2(a) and 2(b).